



Massachusetts Department of Environmental
Protection Bureau of Waste Site Cleanup

BWSC-CAM

Section: V C

28 May 2004

Revision No. 2

Final

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Title: Quality Assurance and Quality Control Requirements and Performance Standards
for SW-846 Method 8151A, Chlorinated Herbicides by Gas Chromatography


WSC – CAM – V C

Quality Assurance and Quality Control
Requirements and Performance Standards for **SW-
846 Method 8151A, Chlorinated Herbicides by
Gas Chromatography Using Methylation or
Pentafluorobenzylation Derivatization**, for the
Massachusetts Contingency Plan (MCP)

Document Status: Final

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Document Chronology

Revision	Status	Date
0	Public Comment Draft	31 January 2002
1	Final	30 May 2003
2	Final	28 May 2004 



Title: Quality Assurance and Quality Control Requirements and Performance Standards
for SW-846 Method 8151A, Chlorinated Herbicides by Gas Chromatography

V. Gas Chromatographic (GC) Methods

C. Quality Assurance/Quality Control (QA/QC) Requirements and Performance Standards for SW-846 Method 8151A, Chlorinated Herbicides by Gas Chromatography

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1.0 QA/QC REQUIREMENTS FOR SW-846 METHOD 8151A

1.1 Method Overview

Method SW-846 8151A is a high resolution gas chromatographic (GC) method that provides extraction, derivatization, and gas chromatographic conditions for the analysis of chlorinated acid herbicides and related compounds in water, soil, and waste samples. Because these compounds are produced and used in various forms (i.e., acid, salt, ester, etc.), Method SW-846 8151A describes a hydrolysis step that can be used to revert environmentally-transformed herbicide esters back into the organic acid prior to analysis.

Samples for analysis are solvent extracted and then esterified with either diazomethane or pentafluorobenzyl bromide. The derivatives produced are then determined by gas chromatography with an electron capture detector (GC/ECD) and the results are reported as acid equivalents.

When using a GC/ECD system, analyses on two columns are required to provide confirmations of identifications. Target analytes may be determined using either narrow-bore or wide bore columns in a single or dual-column configuration.

When SW-846 Method 8151A is used to analyze unfamiliar samples, compound identifications should be supported by at least one additional qualitative technique. Section 7.9 of the Method provides gas chromatograph/mass spectrometer (GC/MS) criteria appropriate for the qualitative confirmation of compound identifications. A narrow-bore column is generally employed for GC/MS confirmation.

1.1.1 Reporting Limits for SW-846 Method 8151A

The reporting limit for SW-846 Method 8151A for chlorinated herbicides is dependent on the choice of sample extraction/derivatization method and the nature of any interferences present. Using standard electron capture detection (ECD), the estimated Reporting Limit (RL) of Method 8151A for determining individual chlorinated herbicides is approximately 5-80 µg/kg (wet weight) for soil/sediment samples and 0.5-2 µg/L for aqueous samples. Somewhat higher RLs may be expected using GC/MS methods. No matter which instrument is used, detection limits for SW-846 Method 8151A will be proportionately higher for sample extracts and samples that require dilution, or when a reduced sample size or final extract volume is used to avoid saturation of the detector.

Sample preservation, container and analytical holding time specifications for surface water, groundwater, soil, and sediment matrices for chlorinated herbicides analyzed in support of MCP decision-making are presented in Appendix V C-1 of this document and Appendix VII-A, CAM-VII A, "Quality Assurance and Quality Control Guidelines for the Acquisition and Reporting of Analytical Data in Support of Response Actions Conducted Under the Massachusetts Contingency Plan (MCP)".



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1.1.2 Additional Requirements

Each laboratory that uses SW-846 Method 8151A is required to operate a formal quality assurance program. The minimum requirements of this program consist of an initial demonstration of laboratory proficiency, ongoing analysis of standards and blanks as a test of continued performance, and the analysis of laboratory control spikes (LCSs) to assess analytical accuracy. Matrix spikes (MS), matrix spike duplicates (MSD) or Matrix duplicates may also be used to evaluate precision when such samples are analyzed either at discretion of laboratory or at request of data-user.

Laboratories must document and have on file an Initial Demonstration of Proficiency for each combination of sample preparation and determinative method being used. These data must meet or exceed the performance standards as presented in Section 1.4 and Table V C-1 of this method. Procedural requirements for performing the Initial Demonstration of Proficiency can be found in SW-846 method 8000B (Section 8.4) and SW-846 Method 8151A (Section 8.3). The data associated with the Initial Demonstration of Proficiency should be kept on file at the laboratory and made available to potential data-users on request. The data associated with the Initial Demonstration of Proficiency for SW-846 Method 8151A must include the following:

QC Element	Performance Criteria
Initial Calibration	CAM-V C, Table V C-1
Continuing Calibration	CAM-V C, Table V C-1
Method Blanks	CAM-V C, Table V C-1
Average Recovery	SW-846 Method 8000, Section 8.4
% Relative Standard Deviation	SW-846 Method 8000, Section 8.4
Surrogate Recovery	CAM-V C, Table V C-1
Internal Standards	CAM-V C, Table V C-1

Note: Because of the extensive analyte list and number of QC elements associated with the Initial Demonstration of Proficiency, it should be expected that one or more analytes may not meet the performance standard for one or more QC elements. Under these circumstances, the analyst should attempt to locate and correct the problem and repeat the analysis for all nonconforming analytes. All nonconforming analytes along with the laboratory-specific acceptance criteria should be noted in the Initial Demonstration of Proficiency data provided

It is essential that laboratory-specific performance criteria for LCS and surrogate recoveries also be calculated and documented. When experience indicates that the criteria recommended in specific methods are frequently not met for some analytes and/or matrices, the in-house performance criteria will be a means of documenting these repeated exceedances. Laboratories are encouraged to actively monitor pertinent quality control performance standards



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described in Table V C-1 to assess analytical trends (i.e., systematic bias, etc) and improve overall method performance by preempting potential non-conformances.

For SW-846 Method 8151A, laboratory-specific control limits must meet or exceed (demonstrate less variability than) the performance standards for each QC element listed in Table V C-1. It should be noted that the performance standards listed in Table V C-1 are based on multiple-laboratory data, which are in most cases expected to demonstrate more variability than performance standards developed by a single laboratory. Laboratories are encouraged to continually strive to minimize variability and improve the accuracy and precision of their analytical results.

This method is restricted to use by, or under the supervision of, analysts experienced in the use of gas chromatographs (GCs), and skilled in the interpretation of gas chromatograms for individual target and multi-component mixtures of chlorinated herbicides in environmental matrices. Each analyst must demonstrate the ability to produce acceptable quantitative and qualitative results both for individual target and multi-component mixtures of chlorinated herbicides with this method.

Special Precaution: Only experienced analysts should be allowed to work with diazomethane due to the potential hazards associated with its use (explosive, carcinogenic).

1.1.3 Sample Extraction/Cleanup Methods

Sample Extraction, Concentration and Derivatization

Samples are normally prepared by one of the following methods prior to gas chromatographic analysis using SW-846 Method 8151A.

Matrix	Method
Air	SW-846 Method 3542 - Modified
Aqueous	Refer to Section 7.3 of SW-846 Method 8151A
Soil/Sediment	Ultrasonic or Shaker Extraction, Refer to Section 7.2 of the Method
Waste	SW-846 Method 3580, Waste Dilution, refer to Section 7.1 of SW-846 Method 8151A
Extract Concentration	Refer to Section 7.4 of SW-846 Method 8151A
Derivatization	Refer to Section 7.5 of SW-846 Method 8151A. Bubbler Method, Section 7.5.1.1 is recommended for samples with low concentrations and the Diazald Kit Method, Section 7.5.1.2 is recommended for soils and samples with high concentrations.



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Extract Cleanup

If additional cleanup of chlorinated herbicide extracts (only applicable to non-hydrolyzed species) is required, refer to Section 7.2.4 of the Method.

1.2 Summary of Method

A measured volume or weight of sample (approximately 1 L for liquids, 30 to 50 grams [dry weight] for solids) is extracted using the appropriate matrix-specific sample extraction technique. Aqueous samples are extracted at a pH > 12.0 with methylene chloride with manual shaking or mechanical techniques. The pH of the extracted sample is adjusted to < 2.0 and extracted with diethyl ether in a separatory funnel. The extract is then concentrated and derivitized prior to analysis.

Solid samples are extracted with a methylene chloride/acetone mixture (1:1 v/v) after acidification with concentrated hydrochloric acid (pH >2.0) or phosphate buffer (2.5 pH). Sample hydrolysis and/or cleanup are applied as necessary as described in Sections 7.2.3 and 7.2.4, respectively. The extract is then concentrated and derivitized prior to analysis. The derivitized extract is analyzed by injecting a 1 to 2- μ L aliquot into a gas chromatograph with a narrow- or wide-bore fused silica capillary column equipped with an electron capture detector.

The chromatographic data produced may then be used to identify and quantify the five (5) individual chlorinated herbicides listed in Table V C-2.

Identification of chlorinated herbicides based on a single-column analysis should be confirmed on a second column, or be supported by at least one other independent qualitative technique. Due caution should be exercised even with dual-column confirmation, however, when highly contaminated samples are processed or during times of high sample throughput. When SW-846 Method 8151A is used to analyze unfamiliar or unusual samples, compound identifications should be supported by another independent qualitative technique. Section 7.9 of the method provides gas chromatographic/mass spectrometer (GC/MS) criteria appropriate for the qualitative confirmation of compound identifications for this purpose.

Dual column confirmation is not required for samples with concentrations of chlorinated herbicides below their respective reporting limit.

1.3 Interferences

Refer to SW-846 Methods 3500B (Sec. 3.0, in particular), 3600C, and 8000B for a general discussion of gas chromatographic interferences. Interferences co-extracted from the samples will vary considerably from matrix to matrix. While general cleanup techniques are referenced or provided as part of this



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method, unique samples may require additional cleanup approaches to achieve desired degrees of discrimination and quantitation. Sources of interference in this method can be grouped into three broad categories.

- Contaminated solvents, reagents, or sample processing hardware,
- Contaminated GC carrier gas, parts, column surfaces, or detector surfaces
- Non-target compounds simultaneously extracted from the sample matrix which cause a detector response, and
- Co-elution of target analytes

An in depth discussion of the causes and corrective actions for all of these interferences is beyond the scope of this guidance document. A brief discussion of the more prevalent interferences is presented below.

1.3.1 Chemical Contaminants

Major contaminant sources for SW-846 Method 8151A include, but are not limited to, contaminated solvents and inadvertent contact of extraction fluids with rubber and/or plastic materials. The use of non-polytetrafluoroethylene (PTFE) thread sealants or plastic tubing should be avoided. It should be noted that interfering contaminants may also be concentrated during sample preparation and cleanup. Analyses of calibration and reagent blanks provide information about the presence of cross-contamination. When potential interfering peaks are noted in blanks, the analyst should review sample pretreatment and concentration procedures to evaluate the source of contamination.

Raw chromatographic data from all blanks, samples, and spikes must be evaluated for interferences. Determine if the source of interference is in the preparation and/or cleanup of the samples and take corrective action to eliminate the problem. **Subtracting blank values from sample results is not permitted.** Such "blank subtraction" is inappropriate and often leads to negative (less than zero) sample results. If the laboratory determines that reporting values without correcting for the blank may result in a false positive result for a sample, the laboratory should fully explain and justify this condition in the laboratory case narrative.

Organic acids, especially chlorinated acids, cause the most direct interferences with the determination by Methylation. Phenols, including chlorophenols, may also interfere with this procedure. The determination using Pentafluorobenzoylation is more sensitive, and more prone to interferences from the presence of organic acids or phenols than by Methylation. Herbicides, being strong organic acids, react readily with alkaline substances and may be lost during analysis. As a precaution, glassware should be acid-rinsed and then re-rinsed to constant pH with organic-free water. **All sodium sulfate used for drying must be acidified.** Other common interferences are presented in Section 3.0 of the Method.



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1.3.2 Cross-Contamination

Contamination by carryover can occur whenever high-concentration and low-concentration samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed with solvent between sample injections. Whenever an unusually concentrated sample is encountered, it should be followed by the analysis of a method or solvent blank to check for cross-contamination.

1.3.3 Special Precautions

- Sample extracts should be scrupulously dried prior to methylation to avoid poor recoveries.
- Alkaline hydrolysis and subsequent extraction of the basic solution removes many chlorinated hydrocarbons and phthalate esters that might otherwise interfere with ECD analysis. However, hydrolysis may result in the loss of Dinoseb and the formation of interfering aldol condensation products, if any residual acetone remains from the extraction of solids.
- The diazomethane solution used must be freshly prepared.
- Esterification duration is critical to the herbicide recoveries. Methylated extracts are subject to trans-esterification and other unwanted side reactions.

1.4 QA/QC Requirements for SW-846 Method 8151A

1.4.1 General Quality Control Requirements for Determinative Chromatographic Methods

Each laboratory that uses SW-846 Method 8151A is required to operate a formal quality assurance program and maintain records to document the quality of all chromatographic data for the GC/ECD system. Refer to SW-846 Method 8000B, Section 7.0 for general operational procedures for all chromatographic methods, including evaluation of retention time windows, calibration verification and chromatographic analysis of samples. The minimum requirements of this program consist of an initial demonstration of laboratory proficiency, ongoing analysis of standards and blanks to confirm acceptable continuing performance, and the analysis of laboratory control spikes (LCSs) and LCS duplicates to assess analytical accuracy and precision as described in SW-846 Method 8151A, Sections 8.0 and 9.0, respectively. Matrix spikes (MS), matrix spike duplicates (MSD) or Matrix duplicates may also be used to evaluate precision when such samples are analyzed either at discretion of the laboratory or at the request of the data-user.

Laboratories must document and have on file an Initial Demonstration of Proficiency for each combination of sample preparation and determinative method being used. These data must meet or exceed the performance standards as presented in Section 1.4 and Table V C-1 of this method. Procedural requirements for performing the Initial



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Demonstration of Proficiency can be found in SW-846 Method 8000B (Section 8.4) and SW-846 Method 8151A (Section 8.3). The data associated with the Initial Demonstration of Proficiency should be kept on file at the laboratory and made available to potential data users on request. The data associated with the Initial Demonstration of Proficiency for SW-846 Method 8151A must include the following:

QC Element	Performance Criteria
Initial Calibration	WSC-CAM–V C, Table V C-1
Continuing Calibration	WSC-CAM–V C, Table V C-1
Method Blanks	WSC-CAM–V C, Table V C-1
Average Recovery	SW-846 Method 8000, Section 8.4
% Relative Standard Deviation	SW-846 Method 8000, Section 8.4
Surrogate Recovery	WSC-CAM–V C, Table V C-1
Internal Standards	WSC-CAM–V C, Table V C-1

1.4.2 Specific QA/QC Requirements and Performance Standards for SW-846 Method 8151A

Specific QA/QC requirements and performance standards for SW-846 Method 8151A are presented in Table V C-1. Strict compliance with the QA/QC requirements and performance standards for this method, as well as satisfying other analytical and reporting requirements will provide an LSP with “Presumptive Certainty” regarding the usability of analytical data to support MCP decisions. The concept of “Presumptive Certainty” is explained in detail in Section 2.0 of WSC-CAM-VII A.

While optional, parties electing to utilize these protocols will be assured of “Presumptive Certainty” of data acceptance by agency reviewers. In order to achieve “Presumptive Certainty”, parties must:

- Comply with the procedures described and referenced in WSC-CAM–V C;
- Comply with the applicable QC analytical requirements prescribed in Table V C-1 for this test procedure;
- Evaluate, and narrate, as necessary, compliance with performance standards prescribed in Table V C-1 for this test method; and
- Adopt the reporting formats and elements specified in the CAM



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In achieving “Presumptive Certainty” status, parties will be assured that analytical data sets:

- ✓ Satisfy the broad QA/QC requirements of 310 CMR 40.0017 and 40.0191 regarding the scientific defensibility, precision and accuracy, and reporting of analytical data;
- ✓ May be used in a data usability assessment, and, if in compliance with all MCP Analytical Method standards, laboratory QC requirements, and field QC recommended limits and action levels, the data set will be considered usable data to support site characterization decisions made pursuant to the MCP; and
- ✓ May be used to support a data representativeness assessment

Widespread adherence to the “Presumptive Certainty” approach will promote inter-laboratory consistency and provide the regulated community with a greater degree of certainty regarding the quality of data used for MCP decision-making. The issuance of these requirements and standards is in no way intended to preempt the exercise of professional judgement by the LSP in the selection of alternative analytical methods. However, parties who elect not to utilize the “Presumptive Certainty” option have an obligation, pursuant to 310 CMR 40.0017 and 40.0191(2)(c), to demonstrate and document an overall level of (laboratory and field) QA/QC, data usability, and data representativeness that is adequate for and consistent with the intended use of the data.



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Table V C-1

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Required QA/QC Parameter	Data Quality Objective	Performance Standard	Required Deliverable	Recommended Corrective Action	Analytical Response Action
Retention Time Windows	Laboratory Analytical Accuracy	(1) Prior to initial calibration and when a new GC column is installed. (2) Calculated according to the method. (Section 7.6 of SW-846 8000).	No	NA	NA
Initial Calibration	Laboratory Analytical Accuracy	(1) Minimum of 5 standards. (2) Low standard must be \leq reporting limit. (3) %RSD should be ≤ 20 or "r" should be ≥ 0.99 . (4) If regression analysis is used, the curve must not be forced through the origin. (5) Curves must be verified by an independent ICV before analysis. (6) All standards must be derivitized using the same procedures used for samples, whether prepared in the laboratory or purchased from a vendor.	No	Recalibrate as required by method.	Report exceedances in case narrative.
Continuing Calibration (CCAL)	Laboratory Analytical Accuracy	(1) Prior to samples, every 12 hours or every 10 samples, whichever is more frequent, and at the end of the analytical sequence. (2) Concentration level near midpoint of curve. (3) Percent difference or percent drift of calibration factors should be ≤ 15 . (4) Verify all analytes fall within retention time windows. (5) All standards must be derivitized using the same procedures used for samples, whether prepared in the laboratory or purchased from a vendor.	No	(1) Perform instrument maintenance, reanalyze CCAL and/or recalibrate as required by method. (2) Reanalyze "associated samples" if beginning or closing CCAL exhibited low response and associated herbicides were or were not detected in samples. (3) Reanalyze "associated samples" if beginning or closing CCAL exhibited high response and associated herbicides were detected in the samples. NOTE: "Associated Samples" refers to all samples analyzed since the last acceptable CCAL.	Report exceedances in case narrative.
Method Blanks	Laboratory Method Sensitivity (contamination evaluation)	(1) Extracted with every batch or every 20 samples, whichever is more frequent. (2) Matrix-specific (e.g., water, soil). (3) Target analytes must be less than or equal to reporting limit.	Yes	Locate source of contamination; correct problem; re-extract associated samples if contaminants are present in the method blank.	(1) Report nonconformances in case narrative. (2) If contamination of method blanks is suspected or present, the laboratory, using a "B" flag or some other convention (such as the case narrative), should qualify the sample results. (3) If re-extraction is performed within holding time, the laboratory may report results of the re-extraction only. (4) If re-extraction is performed outside of holding time, the laboratory must report results of both the initial extraction and re-extraction.

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Required QA/QC Parameter	Data Quality Objective	Performance Standard	Required Deliverable	Recommended Corrective Action	Analytical Response Action
Laboratory Control Spikes (LCSs)	Laboratory Method Accuracy	(1) Extracted with every batch or every 20 samples, whichever is more frequent. (2) Prepared using standard source different than used for initial calibration. (3) Concentration level should be \leq mid-level standard. (4) Must contain all target analytes. (5) Matrix-specific (e.g., soil, water). (6) Percent recoveries must be between 40-140. (7) Laboratories are expected to develop their own in-house control limits, which should fall within the limits listed above.	Yes	Recalculate the percent recoveries. Check MS/MSD; if recoveries are acceptable in MS/MSD, nonconformance may be isolated to LCS. If recoveries are outside criteria in MS/MSD, re-extract associated samples.	(1) Report exceedances in case narrative. (2) If re-extraction is performed within holding time, the laboratory may report results of the re-extraction only. (3) If re-extraction is performed outside of holding time, the laboratory must report results of both the initial extraction and re-extraction.
LCS Duplicate	Laboratory Method Precision	(1) Analyzed with every batch or every 20 samples, whichever is more frequent. (2) Prepared using same standard source and concentration as LCS. (3) Must contain all target analytes. (4) Analyze immediately after LCS. (5) Laboratory-determined percent recoveries must be between 70 – 130 for target compounds (6) Matrix-specific (e.g., soil, water); and (7) Laboratory-determined Relative Percent Difference (RPD) must be ≤ 25 .	Yes	Recalculate RPD; Locate source of problem; Narrate non-conformances	(1) Locate and rectify source of non-conformance before proceeding with the analyses of subsequent sample batches. (2) Narrate non-conformances
MS/MSDs	Method Accuracy in Sample Matrix Method Precision in Sample Matrix	(1) Extracted with every 20 samples (BATCH QC). (2) Matrix-specific. (3) Prepared using standard source different than that used for initial calibration. (4) Concentration level should be between low and mid-level standard. (5) Must contain all target analytes. (6) Percent recoveries should be between 30-150. (7) RPDs should be ≤ 30 for single-component analytes and ≤ 50 for multi-component analytes.	Yes (Only when requested by the data-user)	Check LCS; if recoveries acceptable in LCS, evaluate potential cleanup techniques (Section 7.2.4 of SW-846 8151A) for samples associated with MS/MSD.	Report exceedances in case narrative.

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Required QA/QC Parameter	Data Quality Objective	Performance Standard	Required Deliverable	Recommended Corrective Action	Analytical Response Action
Surrogates	Accuracy in Sample Matrix	<p>(1) Minimum of 1, that encompasses range of temperature program used in method and does not interfere with the target analytes.</p> <p><u>Recommended surrogate: DCAA</u></p> <p>(2) Percent recoveries must be between 30-150 for surrogate on both columns.</p> <p>(3) Laboratories are expected to develop their own in-house control limits, which should fall within the limits listed above.</p> <p>(4) If the surrogate exceeds limits on one column and greater than RL concentrations on both columns are not comparable (RPD > 40), re-extract and re-analyze the sample</p>	Yes (report surrogate recoveries from both columns)	<p>(1) If the surrogate is outside limits on both columns, re-extract and re-analyze the sample.</p> <p>(2) If a surrogate is diluted to a concentration below that of the lowest calibration standard, no corrective action is necessary.</p> <p>(3) If the surrogate exceeds limits on one column only, and the results on both columns are below RLs, no corrective action is necessary.</p> <p>(4) If the surrogate exceeds limits on one column only, and results on both columns are comparable (RPD < 40), then no corrective action is necessary.</p>	<p>(1) Report exceedances in case narrative.</p> <p>(2) If re-extraction or reanalysis yields similar surrogate nonconformances, the laboratory should report results of both extractions or analyses.</p> <p>(3) If re-extraction or reanalysis is performed within holding time and yields acceptable surrogate recoveries, the laboratory may report results of the re-extraction or reanalysis only.</p> <p>(4) If re-extraction or reanalysis is performed outside of holding time and yields acceptable surrogate recoveries, the laboratory must report results of both the initial and re-extraction or reanalysis.</p> <p>(5) If sample is not re-extracted or reanalyzed due to obvious interference, the laboratory must provide the chromatogram in the data report.</p>
Internal Standards (Optional)	Laboratory Analytical Accuracy and Method Accuracy in Sample Matrix	<p>(1) Minimum of 1.</p> <p><u>Recommended Internal Standard: DBOB</u></p> <p>(2) Area counts in samples must be between 50 – 200% of the area counts in the associated continuing calibration standard.</p> <p>(3) Retention times of internal standards must be within calculated retention time windows.</p>	No	If internal standard is outside limits, reanalyze sample unless obvious interference present.	<p>(1) Report exceedances in case narrative.</p> <p>(2) If reanalysis yields similar internal standard nonconformance, the laboratory should report both results of both analyses.</p> <p>(3) If reanalysis is performed within holding time and yields acceptable internal standard recovery, the laboratory may report results of the reanalysis only.</p> <p>(4) If reanalysis is performed outside of holding time and yields acceptable internal standard recovery, the laboratory must report results of both analyses.</p> <p>(5) If sample is not reanalyzed due to obvious interference, the laboratory must provide the chromatogram in the data report.</p>

Title: **Specific QA/QC Requirements and Performance Standards for SW-846 Method 8151A**

Required QA/QC Parameter	Data Quality Objective	Performance Standard	Required Deliverable	Recommended Corrective Action	Analytical Response Action
Identification and Quantitation	Inter-laboratory consistency	(1) Laboratory should use the average calibration factor of each analyte for quantitation. (2) Secondary column analysis: Laboratory must utilize a second dissimilar column to confirm positive herbicide results. The laboratory must report the higher of the two results unless obvious interference is present on one of the columns in which case the laboratory can report the lower result. All required QA/QC parameters (e.g., calibrations, LCSs, etc.) must be met on the secondary column as well. (3) If calibration standards are prepared using methyl esters, the calculation of concentration must include a correction for the molecular weight of the methyl ester versus the acid herbicide.	No	NA	If the RPD between the dual column results exceeds 40, the laboratory should qualify the sample results and/or note the exceedance in the case narrative. <u>NOTE:</u> If the high RPD can be definitively attributed to interference on one of the two columns, the laboratory should report the lower value and provide a discussion in the case narrative that this approach was employed.
General Reporting Issues	NA	(1) The laboratory must report values \geq the sample-specific reporting limit; optionally, values below the sample-specific reporting limit can be reported as estimated, if requested. The laboratory must report results for samples and blanks in a consistent manner. (2) Dilutions: If diluted and undiluted analyses are performed, the laboratory should report results for the <u>lowest</u> dilution within the valid calibration range for <u>each</u> analyte. The associated QC (e.g., method blanks, surrogates, etc.) for each analysis must be reported.	Yes	NA	(1) Qualification of the data is required if reporting values below the sample-specific reporting limit. (2) Recommendation is that the reporting of diluted and undiluted analyses should be a must to be consistent with the inorganic reporting convention of reporting all dilutions and to ensure the lowest possible reporting limit can be achieved if the data is available.

GC = Gas Chromatography
MS/MSDs = Matrix Spikes/Matrix Spike Duplicates
%RSD = Percent Relative Standard Deviation

DCAA = 2,4-Dichlorophenylacetic Acid

“r” = Correlation Coefficient

RPDs = Relative Percent Differences

ICV = Initial Calibration Verification – separate source standard

DBOB = 4,4'-Dibromooctafluorobiphenyl



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1.5 MCP Analyte List for SW-846 Method 8151A

The MCP analyte list for SW-846 Method 8151A, presented in Table V C-2. The list is comprised of ten (10) readily analyzable individual chlorinated herbicides identified in Section 1 of SW-846 Method 8151A. None of these compounds have promulgated MCP Method 1 Groundwater/Soil Standards, as described in 310 CMR 40.0974 and 40.0980, but each has MCP Reportable Concentrations (RCs) as described in 310 CMR 40.0360 and 40.1600 and published EPA Integrated Risk Information System (IRIS) toxicity values. Using available toxicity data, the Department has derived compound-specific MCP Method 2 Groundwater/Soil Standards as described in 310 CMR 40.0983 and 40.0984, respectively. When MCP Method 1 Groundwater/Soil Standards are developed for the compounds listed in Table V C-2, the SW-846 Method 8151A analyte list will be updated accordingly. An updated list of the Department-derived MCP Method 2 Standards may be found at the following URL:

<http://www.mass.gov/dep/bwsc/files/standard/method2/method2.htm>

MCP Method 2 Groundwater/Soil Standards are developed by the Department (or others) for contaminants of concern for which MCP Method 1 Standards have not been promulgated. The use of Department-developed MCP Method 2 Standards is discretionary. Alternatively, site-specific MCP Method 2 Standards may be developed or a Method 3 risk characterization, as described in 310 CMR 40.0990, may be conducted to evaluate or characterize the risk of harm posed by oil or hazardous materials at a disposal site.

1.5.1 Analyte Reporting Requirements for SW-846 Method 8151A

While it is not necessary to request and report all the SW-846 Method 8151A analytes listed in Table V C-2 to obtain Presumptive Certainty, it is necessary to document such a limitation, for site characterization and data representativeness considerations. DEP strongly recommends use of the full analyte list during the initial stages of site investigations, and/or at sites with an unknown or complicated history of uses of oil or hazardous materials. These assessment activities may include but are not limited to:

- Immediate Response Actions (IRAs) performed in accordance with 310 CMR 40.0410;
- Initial Site Investigation Activities performed in accordance with 310 CMR 40.0405(1);
- Phase I Initial Site Investigation Activities performed in accordance with 310 CMR 40.0480 through 40.0483; and
- Phase II Comprehensive Site Investigation Activities performed in accordance with 310 CMR 40.0830

In a limited number of cases, the use of the full analyte list for a chosen analytical method may not be necessary, with respect to data representativeness concerns, including:

- Uncharacterized sites where substantial site/use history information is available to rule-out all but a limited number of contaminants of concern, and where use of the full analyte list would significantly increase investigative costs; or



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for SW-846 Method 8151A, Chlorinated Herbicides by Gas Chromatography

- Well-characterized sites where initial full-analyte list testing efforts have sufficiently narrowed the list of contaminants of concern.

The actual number of chlorinated herbicide compounds analyzed and reported should be based on historical use and/or disposal practices and satisfy Data Quality Objectives (DQOs) of the site assessment.

Note that a desire to avoid detection and quantitation of a contaminant that is present or likely present at a site above background levels is not a valid reason to limit an analyte list, and that such an action could constitute a criminal violation of MGL c. 21E.

In cases where a truncated list of method analytes is selected, laboratories must still employ the method-specific quality control requirements and performance standards associated with the requested analytes list to obtain Presumptive Certainty status.

The Reporting Limit (based on the concentration of the lowest calibration standard) for each contaminant of concern must be less than or equal to the MCP standards or criteria that the contaminant concentrations are being compared to (e.g., Method 2 Standards, RfDs, benchmark values, background, etc.). Meeting “MCP program” reporting limits may require analytical modifications, such as increased sampling weight or volume to increase sensitivity. All such modifications must be described in the Environmental Laboratory case narrative.



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Analyte	CASRN	MCP CLEANUP STANDARDS	
		GW-1	S-1/GW -1
		µg/L (ppb)	µg/g (ppm)
2,5-Dichloro-6-methoxybenzoic acid (Dicamba)	1918-00-9	X ¹	X ¹
2,4-Dichlorophenoxy acetic acid (2,4-D)	94-75-7	X ¹	X ¹
2,4-Dichlorophenoxy butyric acid (2,4-DB) ^a	94-82-6	X ¹	X ¹
2-(2,4-Dichlorophenoxy) propionic acid (Dichloroprop)	120-36-5	X ¹	X ¹
2,2-Dichloro propionic acid (Dalapon)	75-99-0	X ¹	X ¹
2,4-Dinitro-6-sec-butylphenol (Dinoseb)	88-85-7	X ¹	X ¹
2-Methyl-4-chlorophenoxy acetic acid (MCPA)	94-74-6	X ¹	X ¹
2-(2-Methyl-4-chlorophenoxy) propionic acid (MCPB)	93-65-2	X ¹	X ¹
2,4,5- Trichlorophenoxy acetic acid (2,4,5-T)	93-76-5	X ¹	X ¹
2,4,5-Trichlorophenoxy propionic acid (Silvex)	93-72-1	X ¹	X ¹

CASRN – Chemical Abstract Service Registry Number

1. Department-Developed MCP Method 2 Standard. Use of these Standards is discretionary

a. Co-elutes with 4-(2-Methyl-4-chlorophenoxy) butyric acid (MCPB)



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2.0 Data Usability Assessment for SW-846 Method 8151A

Overall data usability is influenced by uncertainties associated with both sampling and analytical activities. This document provides detailed quality control requirements and performance standards for SW-846 Method 8151A which may be used to assess the analytical component of data usability. The sampling component of data usability, an independent assessment of the effectiveness of sampling activities to meet data quality objectives, is not substantively addressed in this document

3.0 Reporting Requirements for SW-846 Method 8151A

3.1 General Reporting Requirements for SW-846 Method 8151A

General environmental laboratory reporting requirements for analytical data used in support of assessment and evaluation decisions at MCP disposal sites are presented in CAM-VII A, Section 2.4. This guidance document provides recommendations for field QC, as well as the required content of the Environmental Laboratory Report, including:

- Laboratory identification information presented in CAM-VII A, Section 2.4.1,
- Analytical results and supporting information in CAM-VII A, Section 2.4.2,
- Sample- and batch-specific QC information in CAM-VII A, Section 2.4.3,
- Laboratory Report Certification Statement in CAM-VII A, Section 2.4.4,
- Copy of the Analytical Report Certification Form in CAM-VII A, Exhibit VII A-1,
- Environmental Laboratory Case Narrative contents in CAM-VII A, Section 2.4.5,
- Chain of Custody Form requirements in CAM-VII A, Section 2.4.6

3.2 Specific Reporting Requirements for SW-846 Method 8151A

Specific Quality Control Requirements and Performance Standards for SW-846 Method 8151A are presented in Table V C-1. Specific reporting requirements for SW-846 Method 8151A are summarized below in Table V C-3 as "Required Analytical Deliverables (**YES**)". These routine reporting requirements should always be included as part of the laboratory deliverable for this method. It should be noted that although certain items are not specified as "Required Analytical Deliverables (**NO**)", these data are to be available for review during an audit and may also be requested on a client-specific basis.



Title: Routine reporting Requirements and Performance Standards for SW-846 Method 8151A,
Chlorinated Herbicides by Gas Chromatography

Parameter	Required Analytical Deliverable
Retention Time Windows	NO
Initial Calibration	NO
Continuing Calibration (CCAL)	NO
Method (Preparation) Blank	YES
Laboratory Control Spikes (LCSs)	YES
LCS Duplicates	YES
Matrix Spike (MS)	YES (if requested field MS)
Matrix Spike Duplicate (MSD)	YES (if requested field MS/MSD)
Matrix Duplicate (MD)	<i>YES (if requested by Data User)</i>
Surrogates	YES
Internal Standards (ISs)	NO
Identification and Quantification	NO
General reporting Issues	YES



Title: Summary of Minimum Field QC Sample Frequency in Support of “Presumptive Certainty” Status for Chlorinated Herbicides by SW-846 Method 8151A

Sample preservation, container and analytical holding time specifications for surface water, groundwater, soil, and sediment matrices for chlorinated herbicides analyzed in support of MCP decision-making are summarized below and presented in Appendix VII-A of CAM-VII A, “Quality Assurance and Quality Control Guidelines for the Acquisition and Reporting of Analytical Data in Support of Response Actions Conducted Under the Massachusetts Contingency Plan (MCP)”.

Matrix	Container ¹	Preservation	Holding Time ²
Aqueous Samples, with no Residual Chlorine	(2) 1-L amber glass bottles w/ Teflon-lined screw caps	Cool to 4°C	7 days to extraction; 40 days from extraction to analysis ³
Aqueous Samples, with Residual Chlorine ⁴	(2) 1-L amber glass bottles w/ Teflon-lined screw caps	Add 1-mL 10% sodium thiosulfate solution per container (or 0.008%) ⁵ . Addition of thiosulfate solution to sample container may be performed in the laboratory prior to field use. Cool to 4°C	7 days to extraction; 40 days from extraction to analysis
Soil/Sediment Samples	(1) 8-oz. amber glass jar w/ a Teflon-lined screw cap	Cool to 4°C	14 days to extraction; 40 days from extraction to analysis
Waste Samples	(1) 500 mL amber wide mouth jar with a teflon lined screw cap.	No special preservation required	14 days to extraction; 40 days from extraction to analysis

1 The number of sampling containers specified is not a requirement. For specific analyses, the collection of multiple sample containers is encouraged to avoid resampling if sample is consumed or compromised during shipping and/or analysis

2 Holding time begins from time of sample collection.

3 Store sample extracts at – 10° C, protect from light, and store in sealed vials (e .g., screw-cap or crimp-caped vials) with un-pierced PTFE-lined septa. See SW-846 Method 8270C, Section 6.1.

4 Presence of chlorine residual is usually associated with drinking water samples

5 Confirm dechlorination. If Residual Chlorine > 5 mg/L additional dechlorination agent may be required